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(54) Title: PHOTINITIATORS

(57) Abstract

A compound for use as a photoinitiator comprises a photoreactive portion and a pendent group, said photoreactive portion including an aromatic moiety and said pendent group incorporating at least one optionally-substituted poly(alkylene glycol) moiety. Preferred photoreactive portions include optionally-substituted benzophenone, thioxanthone and anthraquinone compounds substituted by a polyethylene glycol or polypropylene glycol moiety of average molecular weight in the range 150 to 900. Compounds of the type described are found to have low migration from cured films.

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PHOTOINITIATORS

5 This invention relates to photoinitiators and particularly, although not exclusively, relates to novel compounds for use as photoinitiators.

10 Photoinitiated curing processes may use photoinitiators which generate photo-excited species, which react with the curing agents, commonly called synergists, to produce radicals which are thought to be the species responsible for the polymerisation reaction. Commonly the curing agents are aromatic tertiary amines. Commercial amine curing agents are ethyl-4-(N,N'-15 dimethylamino) benzoate (EDB) and 2-n-butoxyethyl 4-(dimethylamino) benzoate (BEDB).

20 Photoinitiators which are available, and suitable for use with amine curing agents, are thioxanthone initiators, in particular isopropylthioxanthone (ITX); anthraquinone initiators; and benzophenone initiators, in particular 2-methylbenzoylbenzoate (2-MBB).

25 Other types of photoinitiators, referred to as Type I photoinitiators include, for example, benzoin and benzoin derivatives. They may be used alone in a photoinitiated reaction or in combination with an amine compound which may act as an oxygen scavenger.

30 Japanese published patent application 6263814 (Toyo Ink) proposes photoinitiators obtained by reacting dihydric polyol compounds with ortho-benzoylbenzoic acid. These are said to be of use in curable coating compositions said to have reduced odour, and to be free from deterioration from curability. However, in 35 experiments we have found the di(benzoyl benzoate)

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compound of this type produced by reacting ortho-benzoylbenzoic acid with poly(ethylene glycol)<sub>300</sub> to migrate from a cured polymer at a relatively high rate.

5 One major problem associated with known photoinitiators is the relative ease of migration of the photoinitiator from cured polymer since this results in adjacent materials being tainted. When the polymer is, for example, a film and the adjacent materials are, for  
10 example, foodstuffs, this is very undesirable.

This invention is based on the discovery that a photoinitiator can be rendered less susceptible to migration by substitution with groups as described herein.

15

In accordance with a first aspect of the invention, there is provided a compound for use as a photoinitiator, comprising a photoreactive portion and a pendent group, said photoreactive portion including an aromatic moiety  
20 and said pendent group incorporating at least one optionally-substituted poly(alkylene glycol) moiety.

No claim is made herein to the compounds described in applicant's co-pending application number PCT/GB96/00911.

25

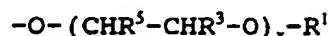
Unless otherwise stated, optional substituents described herein include halogen atoms, especially chlorine atoms, and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups;

Unless otherwise stated, alkyl groups may have up to ten carbon atoms, preferably up to seven carbon atoms,

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more preferably up to four carbon atoms. Preferred alkyl groups include methyl and ethyl groups.

5 Preferably, said optionally substituted poly(alkylene glycol) moiety is of general formula



I

10 wherein  $R^1$  represents an optionally substituted alkyl group,  $R^3$  and  $R^5$  independently represent a hydrogen atom or an optionally substituted alkyl group and  $x$  represents an integer.

15 Preferably,  $R^1$  represents an unsubstituted alkyl group. Preferably,  $R^1$  represents a  $C_{1-6}$  alkyl group, more preferably a  $C_{1-4}$  alkyl group. Especially preferred is the case wherein  $R^1$  represents a methyl or ethyl group.

20 Preferably,  $R^3$  and  $R^5$  independently represent a hydrogen atom or an unsubstituted alkyl group. When  $R^3$  represents an alkyl group,  $R^5$  preferably represents a hydrogen atom. Preferably,  $R^3$  represents a hydrogen atom or an alkyl group and  $R^5$  represents a hydrogen atom. More preferably, both  $R^3$  and  $R^5$  represent hydrogen atoms.

25 Integer  $x$  may have a mean value of greater than 3, suitably greater than 4, preferably greater than 5, more preferably greater than 6. Integer  $x$  may have a mean value of less than 20, suitably less than 15, preferably less than 11, more preferably less than 9.

30

Said optionally-substituted poly(alkylene glycol) moiety may have an average molecular weight (excluding any optional substituents) of at least 150, suitably 200, preferably 250, more preferably 300, especially 340. Said

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average molecular weight may be less than 900, suitably 800, preferably 700, more preferably 600, especially 500.

5 Said moiety of general formula I may be linked directly to said photoreactive portion via the ether-oxygen atom thereof or may be linked to said photoreactive portion by a linking group arranged between said photoreactive portion and said moiety of formula I.

10 A said linking group may include a first moiety of general formula  $-\text{OCR}^2\text{CO}-$  wherein groups  $\text{R}^2$  may be the same or different and may represent a hydrogen atom or an optionally substituted, preferably unsubstituted, alkyl group. Preferably, each  $\text{R}_2$  represents a hydrogen atom.

15 A said linking group may include a group  $-\text{CO}-$ , instead of said first moiety.

20 Said linking group may include an intermediate moiety between said photoreactive portion and said first moiety or group  $-\text{CO}-$ . An intermediate moiety may include a phenyl group and may comprise a group  $-\text{S-Ph-}$  wherein the sulphur atom is bonded to said photoreactive portion and "Ph" represents an optionally-substituted, especially an unsubstituted, phenyl group.

25 Preferably, said linking group comprises said first moiety wherein the ether oxygen atom of said moiety is bonded to said photoreactive portion.

30

The or each pendent group is preferably an aliphatic group.

35 Preferably, said photoreactive portion incorporates an optionally substituted phenylcarbonyl moiety. The

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carbonyl group of said optionally substituted phenyl carbonyl moiety may be bonded to another moiety which may comprise an optionally-substituted phenyl or alkyl moiety. Where it comprises an optionally-substituted phenyl moiety, said moiety may, in turn, be bonded to the phenyl group of said phenylcarbonyl group by an intermediate atom or group which may comprise a group -CO- or -S- thereby to define a ring structure, for example of thioxanthone or anthraquinone. Preferred optional substituents on said 10 optionally-substituted phenyl group include optionally-substituted thioalkyl or thiophenyl groups.

Where said optionally substituted phenyl carbonyl moiety is substituted by an optionally-substituted alkyl group, said group is preferably unsubstituted or substituted by a hydroxy group. A preferred alkyl group has a general formula -CR<sup>6</sup>R<sup>7</sup>OH where R<sup>6</sup> and R<sup>7</sup> independently represent an optionally-substituted alkyl group or together define a ring, for example a cycloalkyl, 20 especially a cyclohexyl ring.

Said photoreactive portion may be selected from optionally-substituted benzaldehyde, benzophenone, anthraquinone, thioxanthone, thiophenylbenzophenone 25 (especially 4-(thiophenyl)benzophenone) and benzoin derivatives.

Preferred benzaldehyde derivatives include 1-hydroxy-cyclohexyl-phenyl ketone,  $\alpha, \alpha$ -dimethoxy- $\alpha$ -hydroxy acetophenone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, benzoyl-diphenyl-phosphine 30 oxide and methyl  $\alpha$ -oxobenzeneacetate derivatives.

Said pendent group may be bonded to said benzaldehyde 35 derivatives in any suitable position. It is preferably

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bonded to the phenyl group in the case of 1-hydroxy-cyclohexyl-phenyl ketones,  $\alpha, \alpha$ -dimethoxy- $\alpha$ -hydroxy acetophenone, methyl  $\alpha$ -oxobenzeneacetate and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one derivatives. It is preferably bonded to the benzoyl group in the case of benzoyl-diphenyl-phosphine oxide derivatives.

Where said photoreactive portion is a benzophenone derivative, said derivative is preferably substituted by one or two pendent groups as described above, said groups suitably being substituted at the 4- and/or 4'- positions.

Where said photoreactive portion is an anthraquinone or thioxanthone derivative, said derivative is preferably substituted by one or two pendent groups as described above, said groups suitably being substituted at the 1- and/or 8- positions. In one embodiment, a thioxanthone derivative may be substituted by a pendent group at the 1-position and a halogen, especially a chlorine atom, at another position, especially the 4- position.

Where said photoreactive portion is a thiophenylbenzophenone derivative, said thiophenyl group of said derivative may be substituted by a said pendent group as described above, preferably at the 4- position.

Preferred benzoin derivatives include benzoin per se, benzoin ethers, for example benzoin ethyl ether, isopropyl ether, n-butyl ether and i-butyl ether, and benzilketals. Such benzoin derivatives may be substituted by one or two pendent groups as described above. For example, said benzoin derivatives may be substituted on the benzene rings, or the hydroxy group of benzoin may be substituted with a said pendent group.

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A benzilketal may be substituted on the benzene rings or on the ketal carbon atom.

Preferably, said photoreactive portion is selected  
5 from optionally substituted, more preferably mono-  
substituted or unsubstituted, benzophenone, anthraquinone  
and thioxanthone; or from a group of general formula Z-CO-  
Ph wherein Z represents an optionally-substituted alkyl  
10 group and Ph represent an optionally-substituted phenyl  
group.

In accordance with a second aspect of the present invention, there is provided a process for the preparation of a compound according to said first aspect, the process  
15 comprising:

(a)(i) reacting a compound corresponding to said photoreactive portion but including one or more active atoms or groups with a precursor of said pendent group so  
20 that said precursor replaces said active atom or group;  
and

(ii) optionally derivatising said precursor of said pendent group; or  
25

(b)(i) reacting a compound which includes a moiety corresponding to a first portion of said photoreactive portion but including an active atom or group, with a precursor of said pendent group so that said precursor  
30 replaces said active atom or group;

(ii) reacting the product of step (b)(i) with a moiety corresponding to a second portion of said photoreactive portion; and

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iii) optionally derivatising said precursor of said pendent group.

5 Preferably, said active atoms or groups are selected from halogen atoms or hydroxy or alkoxy groups.

10 In one embodiment, in step a(i), said photoreactive portion preferably includes one or more hydroxy groups at each position wherein it is desired to provide a said pendent group. Each said precursor of said pendent group which is to be reacted preferably includes a halogen atom, especially a bromine atom, which activates said precursor and enables the oxygen atom of a said hydroxy group to attack the carbon atom bearing the halogen atom in a 15 nucleophilic substitution reaction. The reaction is suitably carried out in an aprotic solvent, in the presence of a base, suitably an inorganic base, under reflux.

20 In one example according to said first embodiment, the precursor used in step a(i) may correspond to said pendent group in said compound of the first aspect in which case step a(ii) may not be required. Alternatively, the precursor used in step a(i) may need further 25 derivatisation to provide said pendent group of said compound of the first aspect. In this case, the compound used in step (a)(i) may comprise a precursor with two active atoms or groups, for example a halogen, especially a bromine atom as described above and an ester group. Then 30 in step (a)(ii), said ester group may be transesterified to provide the desired pendent group.

35 In a preferred example according to said first embodiment, a photoreactive portion including one or more hydroxy groups is reacted with a precursor which includes

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a bromine atom and an ester group. The bromine atom activates the precursor which reacts with a said hydroxy group to form an ether linkage. The ester group can then be transesterified with an optionally substituted 5 poly(alkylene glycol) moiety to produce the desired compound. The transesterification process may be carried out under standard conditions.

In a second embodiment of step a(i), a salt of a 10 hydroxy derivative corresponding to said photoreactive portion is reacted with a halogenated, especially a chlorinated, compound corresponding to the desired pendent group.

15 Process (a) is the preferred process for preparation of most of the compounds of the first aspect. Process (b) may be used for the preparation of compounds which include complex photoreactive portions.

20 In step (b)(i), said first portion may be activated by means of an alkoxide group and may be reacted with a precursor group activated, for example, by a tosylate group. A second active group on said first portion may be derivatised and/or further reacted with a suitably 25 activated second portion of said photoreactive portion. For example, process (b) may be used for the preparation of thiophenylbenzophenone derivatives by reacting potassium 4-nitrophenoxy with methoxy poly(ethylene glycol) tosylate, followed by reduction of the nitro group 30 to an amine which can then be diazotised and reacted with sodium sulphide to produce a thiophenyl derivate. The thiophenyl derivative can then be reacted with suitably activated, for example by a chlorine atom, benzophenone to produce the desired compound.

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Other compounds which fall within the scope of the present invention are commercially available and/or may be prepared by derivatising commercially available compounds using processes analogous to those described herein.

5

Starting materials for the preparation of compounds in accordance with said second aspect are commercially available and/or may be prepared by standard procedures from readily available materials.

10

The invention extends to the use of a compound according to said first aspect in a polymerisation reaction.

15

In accordance with a further aspect of the present invention, there is provided a polymer curing composition, which may be in kit form, comprising a compound according to said first aspect, together with a curing agent with which the compound of general formula I may react, when 20 irradiated, to generate a polymerisation specie, for example a radical.

25

In accordance with a further aspect of the present invention, there is provided a polymerisable composition comprising a polymerisable material suitably present in an amount from 80 to 99 wt% and a compound of the first aspect, suitably present in an amount from 20 to 1 wt. %.

30

The composition may further include a curing agent, suitably present in an amount from 14 to 2 wt%. Preferably, said polymerisation material is present in an amount from 80 to 97 wt% and said compound of the first aspect is present in an amount from 6 to 1 wt%. 5 wt% or less, preferably 4 wt% or less, more preferably 3 wt% or 35 less of said compound of said first aspect may be present.

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In accordance with a further aspect of the present invention, there is provided a polymeric composition prepared using a compound according to said first aspect or said polymerisable composition by photo-curing.

5

A suitable curing agent may, for example, be an aromatic amine compound, for example ethyl-4-(N,N'-dimethylamino) benzoate (EDB) or 2-n-butoxyethyl 4-(dimethylamino) benzoate (BEDB) or a curing agent 10 described in our PCT patent application number PCT/GB96/00910 or a co-filed application entitled Amine Compounds. The contents of both applications are incorporated herein by reference.

15

A suitable polymerisable material is any material whose polymerisation can be initiated by a radical, especially an amine radical. Preferably the polymerisation is applied to acrylate systems where the polymerisable material (monomer) may, for example be 1,6-20 hexanediol diacrylate (HDDA), 2-hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and methyl methacrylate (MMA).

25

The polymerisable materials may be suitable for surface/coating/film applications. They may be formulated with other components, including inks, for printing applications.

30

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

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The invention will now be further described, by way of example, with reference to the following figures, wherein:

5       Figure 1 is a graph of % migration versus number of passes of a Colordry lamp for compounds 1, 2 and C1 described hereinafter;

10      Figure 2 is a graph of absorbence versus number of passes for compounds 3, C2 and C3 described hereinafter;

15      Figure 3 is a graph of % migration versus number of passes of a Colordry lamp for the compounds shown in figure 2.

20      Figures 4, 6, 8, 10 and 13 are graphs of absorbence versus number of passes for respective sets of examples (3, 4, 5, C3, C6), (8, 9), (C7, C8, 11), (6) and (C10, 12, 13, 14);

25      Figures 5, 7, 9, 12 and 14 are graphs of % migration versus number of passes for respective sets of examples (3, 4, 5, C3, C6), (8, 9), (C7, C8, 11), (C9, 7) and (C10, 12, 13, 14).

30      Figure 11 is a graph of % extent of reaction versus time (secs) for compounds 7 and C9, as assessed using RTIR.

35      Preparation of photoinitiators of the invention

Compound 1 : Di(monomethylpolyethyleneglycol),,ester of 4,4'-di(carboxymethoxy)benzophenone.

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Step 1

4,4'-Dihydroxybenzophenone (2.000g; 0.01 moles), ethyl bromoacetate (4.175g; 0.025 moles), dry potassium carbonate (3.455g) and dry acetone (70ml) distilled from lithium aluminium hydride were refluxed together for 48 hours. The salt was filtered and the solvent and excess ethylbromoacetate were removed under vacuum. The solid product was recrystallised from ethanol.

Melting point 100 - 102°C

10 Yield 5.60g (72.5%)

Elemental analysis: C<sub>21</sub>H<sub>22</sub>O, %calc: C = 65.26, H = 5.74; % found: C = 65.41; H = 5.85.

The product structure was confirmed by 100MHz proton NMR, in CDCl<sub>3</sub>, solvent, the results being as follows:

15 1.4 ppm, t, 6H, ester methyl group;

4.5 ppm, q, 4H, ester -CH<sub>2</sub>,

4.85 ppm, s, 4H, ether -CH<sub>2</sub>-;

7.00-8.00 ppm, AA'BB' aromatic system, 8H, aromatic.

20 Step 2

The product of Step 1 was transesterified in toluence under reflux with poly(ethylene glycol)<sub>350</sub>monomethylether in a dry environment using a Tilcom BIP catalyst (butyl isopropyl titanate) to give a viscous orange product. The 25 product was left under high vacuum for 24 hours in an attempt to remove all traces of toluene and characterised by HPLC and proton NMR in CDCl<sub>3</sub>, the results being as follows:

30 HPLC : Two sets of peaks corresponding to mono- and di- substituted PEG compounds after 5 hours reflux. The peaks convert to one set of peaks (under the same conditions) after a further 5 hours reflux.

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NMR:

1.30 ppm unidentified doublet  
3.35 ppm s, 6H, ether CH<sub>3</sub>  
3.60 ppm s, 60H, PEG-CH<sub>2</sub>  
5 4.65 ppm s, 4H, ether CH<sub>2</sub>  
6.80 - 7.80 ppm, AA'BB' splitting, 8H, aromatic  
protons.

10 Compound 2 : Di(monomethylpolyethylene glycol)<sub>350</sub>ester  
of 1,8-di(carboxymethoxy)anthraquinone.

Step 1

15 Step 1 of the process described above for the preparation of compound 1 was repeated except that 4,4'-dihydroxybenzophenone was replaced with 1,8-dihydroxyanthraquinone. The resulting compound was characterised as follows:

20 Melting point 124-126°C  
Yield 25.30g (75.78%)  
Elemental analysis C<sub>22</sub> H<sub>20</sub> O<sub>8</sub> %calc: C= 64.07, H= 4.89;  
25 %found : C= 63.57, H= 4.63.  
The product structure was confirmed by 60 MHz proton NMR, in CDCl<sub>3</sub> solvent, the results being as follows:  
1.40 ppm, t, 6H, -CH<sub>3</sub>;  
4.40 ppm, q, 4H, ester -CH<sub>2</sub>-;  
5.00 ppm, s, 4H, ether -CH<sub>2</sub>-;  
7.30 - 8.20 ppm, m, 6H, aromatic.

Step 2

30 Step 2 of the process described above for compound 1 was repeated, using the product of latter mentioned Step 1. The resulting compound was characterised as follows:  
HPLC : a single set of peaks was recorded, indicating disubstitution of the PEG compound had taken place.

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NMR:

3.30 ppm, s, 6H, -CH<sub>3</sub>;  
3.60 ppm, s, 60H, PEG-CH<sub>2</sub>-;  
4.85 ppm, s, 4H, ether-CH<sub>2</sub>-;  
5 7.10-7.80 ppm, m, 6H, aromatic.

Compound 3 : a mixture comprising  
(monomethylpolyethylene glycol)<sub>350</sub>ester of 2-carboxymethoxy  
thioxanthone and (monomethylpolyethylene glycol)<sub>350</sub>ester of  
10 4-carboxymethoxy thioxanthone.

Step 1

15 Step 1 of the process described above for the preparation of compound 1 was repeated except that 4,4'-dihydroxybenzophenone was replaced with a mixture of 2- and 4-hydroxy thioxanthone. The resulting compound was characterised as follows:

Melting point 81-82°C  
Elemental analysis C<sub>17</sub>H<sub>14</sub>O<sub>4</sub>S %calc : C=64.95, H= 4.49  
20 %found: C= 64.85; H= 4.41.  
The product structure was confirmed by 100MHz proton NMR, in CDCl<sub>3</sub> solvent, the results being as follows:  
1.30 ppm, t, 3H, -CH<sub>3</sub>;  
4.30 ppm, q, 2H, -CH<sub>2</sub>- (ester);  
25 4.90 ppm, s, 2H, -CH<sub>2</sub>- (ether);  
7.30 - 8.80 ppm, m, 7H, aromatic.

Step 2

30 Step 2 of the process described above for compound 1 was repeated, using the product of the latter mentioned Step 1. The resulting compound was characterised as follows:

NMR:  
3.40 ppm, s, 3H, -OMe;  
35 3.60, s, 26H, -CH<sub>2</sub>CH<sub>2</sub>-;

- 16 -

4.80, s, 2H, -CH<sub>2</sub>CO<sub>2</sub>-;  
7.25 - 8.55, m, 7H, aromatic.

HPLC: A single set of peaks was obtained indicating one PEG chain had been appended.

5

Compound 4: (Monomethylpolyethylene glycol)<sub>350</sub> ester of 4-carboxymethoxythioxanthone

10 The product structure was confirmed by 100 MHz proton NMR, in CDCl<sub>3</sub> solvent, the results being as follows:

Steps 1 and 2

15 These were as described in Example 3, except that 4-hydroxythioxanthone was used as a starting material instead of 4,4'-dihydroxybenzophenone.

3.40 ppm, s, 3H, -ome;  
3.65 ppm, s, 25H, -CH<sub>2</sub>CH<sub>2</sub>-;  
4.86, s, 2H, -CH<sub>2</sub>CO<sub>2</sub>;  
7.20-8.40, m, 7H, aro.

20 RP-HPLC retention time in minutes was 19.23 - 55.93. This shows that no starting material was present.

Compound 5: (Monomethylpolyethylene glycol)<sub>350</sub> ester of 1-chloro-4-carboxymethoxythioxanthone

25

Step 1

4-chloro-1-hydroxythioxanthone was prepared as follows:

30 Sulphuric acid (98%; 193 ml) and water (10 ml) were stirred vigorously at ambient temperature and dithio-bis-benzoic acid (DTBBA) (20g) was added over 60 minutes followed by stirring for 90 minutes. 4-chlorophenol (33.43g) was added over 30 minutes at ambient temperature and the mixture was stirred overnight at 15 - 20°C followed  
35 by heating at 70°C for 8 hours. The mixture was then cooled

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and diluted (with cooling) with cold water (300 ml). Further dilution with water resulted in a yellow precipitate which was filtered. The crude residue was slurred with 4M sodium hydroxide solution which resulted 5 in a blood red mixture. Filtration of the mixture, followed by adding the residue to water and subsequent acidification with conc HCl yielded a bright yellow precipitate which was collected and dried over silica under vacuum. Water of crystallisation was removed from 10 the product.

The resulting compound was characterised as follows:  
Melting point - 249 - 251°C

Mass spectrum parent ion - 262.0

15 IR spectrum (cm<sup>-1</sup>) - OH str, 3257  
- diaryl C=Ostr, 1633.4  
- C-Ostr, 1312.

20 <sup>1</sup>H nmr (in ppm) - 3.70, bs, water  
- 7.00 - 8.30, m, 6H, aro  
- 11.45, s, 1H, -OH

Elemental analysis C<sub>13</sub>H<sub>7</sub>ClO<sub>2</sub>S % calc : C=59.42, H=2.69;  
% found: C = 58.37, H = 2.59.

25 Steps 2 and 3

The product of Step 1 was treated as described in Example 1, Steps 1 and 2 to prepare the desired compound which was characterised as follows:

30 IR spectrum (cm<sup>-1</sup>) 630, C-S str, weak  
1671, C = Ostr, ketone  
1755, C = Ostr, ester

35 <sup>1</sup>H nmr (in ppm) - 3.30, s, 3H, -OMe;  
3.60, s, 30H, -CH<sub>2</sub>CH<sub>2</sub>-  
4.80, s, 2H, -OCH<sub>2</sub>CO<sub>2</sub>-  
6.80 - 8.375, m, 6H, aro

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UV spectrum ( $\lambda$  max in nm/magnitude in abs units)

- 389/0.074  
- 312/0.12  
- 257/0.51

5 RP-HPLC retention time in minutes 30.75 - 58.10.

10 Compound 6: a mixture consisting essentially of (monomethylpolyethylene glycol)<sub>350</sub> ether of 2- and 4-thioxanthone

10

Step 1

15 The chloro derivative of monomethylpolyethylene glycol-350 was prepared by reacting thionyl chloride with commercially available monomethyl PEG-350 as described in US 4 602 097 except that dimethylformamide referred to was replaced with a slight molar excess of pyridine and, in the process, the thionyl chloride solution was added with cooling, and subsequent heating at 40°C for 10 hours was used instead of refluxing. Overnight, the pyridine 20 hydrochloride salt separated and the desired chloro derivative was decanted. Infra-red analysis showed the absence of an O-H stretch in the product.

25

Step 2

25 The sodium salt of hydroxythioxanthone was prepared by addition of the corresponding hydroxythioxanthone to methanol followed by addition of solid sodium methoxide. Confirmation of salt formulation was by a change of colour from yellow to blood red. The product was evaporated to 30 dryness to yield a brick-red solid that was used without further purification.

Step 3

35 The title compound was prepared by reacting the products of Step 1 and 2 together in dimethylformamide.

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Sodium chloride precipitated the mixture was filtered and the desired product isolated by standard techniques.

5      Compound 7: Di-[polyethylene glycol]<sub>350</sub> monomethylether anthraquinone -1,4-dicarboxylate

This was prepared using a process as described for compound 2, starting with 1,4-dihydroxyanthraquinone.

10      Compound 8: (Monomethylpolyethylene glycol)<sub>350</sub> ester of (4-thiophenyl-4-carboxymethoxy)benzophenone

Step 1: Preparation of 4-chloro-4'-methoxybenzophenone  
4-chloro-4'-hydroxybenzophenone (46.60g), sodium  
15      hydroxide (10g) and water (200ml) were stirred and cooled to 5°C. Dimethyl sulphate (19ml) was added dropwise over 90 minutes, followed by stirring at ambient temperature for 30 minutes and refluxing for 3 hours to yield a yellow precipitate. The mixture was diluted with water (200ml)  
20      and extracted with dichloromethane. The organic phase was extracted with dilute base (e.g. sodium carbonate) and water, followed by drying over sodium sulphate. The solvent was removed and the solid residue was recrystallized from methanol. Characterising data is  
25      provided in Table 2.

Step 2: Preparation of 4-thiophenyl-4'-methoxybenzophenone  
The product of Step 1 (5g) and potassium carbonate (5g) were stirred at ambient temperature under nitrogen in  
30      dry DMF. Thiophenol (2.05ml) was added dropwise over 45 minutes and the mixture stirred at 25°C for 4 hours, and then at 60°C for 12 hours, followed by dilution with water (200ml) and extraction using benzene. The organic phase was washed repeatedly with dilute base and water prior to  
35      drying over sodium sulphate. The solvent was then removed

- 20 -

and the solid residue was recrystallized from methanol. Characterizing data is provided in Table 2.

5 Step 3: Preparation of 4-thiophenyl-4'-hydroxybenzophenone.

The product of Step 2 (1.25g) was added to hydrogen bromide (40%aq solution; 20ml) and glacial acetic acid (20ml) and refluxed for 30 minutes. Acetic anhydride (20ml) was added with cooling, followed by refluxing for 10 3 hours. Acetic acid was removed under vacuum and the residue was added to water (50ml) which was extracted with dichloromethane. The organic phase was extracted with sodium hydroxide solution (0.5M) and acidified to yield an ivory precipitate which was filtered and recrystallized 15 from methanol/water (2:1). Characterising data is provided in Table 2.

20 Step 4: Preparation of ethylester of (4-thiophenyl-4'-carboxymethoxy)benzophenone

The product of Step 3(3g), potassium carbonate (3g), ethylbromoacetate (2.22ml) and acetone (50ml) were refluxed for 36 hours. The salt was filtered and the solvent and excess ethylbromoacetate removed under vacuum to yield a white solid which was recrystallized from 25 ethanol. Characterizing data is provided in Table 2.

30 Step 5: Preparation of (monomethylpolyethyleneglycol)<sub>350</sub> ester of (4-thiophenyl-4-carboxymethoxy)benzophenone

The product of Step 4 (2g) and polyethyleneglycol monomethylether ( $M_n$  350) (1.8g) were azeotroped in xylene for 2 hours under a nitrogen atmosphere. The solution was cooled and two drops of titanium tetrakisopropoxide added followed by refluxing for 6 hours. The solvent was removed under vacuum to yield a light brown liquid which

- 21 -

was purified by column chromatography. Characterizing data is provided in Table 2.

5 Compound 9: (Monomethylpolyethyleneglycol)<sub>350</sub> ester of (4-methylthio-4-carboxymethoxy)benzophenone

Step 1: Preparation of 4-methylthio-4'-methoxybenzophenone

Thioanisole (42ml) and dichloromethane (50ml) were stirred at 5°C and aluminium chloride (26g) added slowly. 10 Benzoyl chloride (25g) was added dropwise over 30 minutes and the reaction mixture stirred at 60°C for 6 hours trapping any HCl generated. The warm reaction mixture was poured onto concentrated HCl (100ml) and ice (100g). The aqueous mixture was extracted with toluene and the organic 15 phase washed with dilute base and water, followed by drying over sodium sulphate. Removal of the solvent yielded a white solid which was recrystallized from methanol. Characterizing data is provided in Table 3.

20 Step 2: Preparation of 4-methylthio-4'-methoxybenzophenone

The product of Step 1 (8g) was added to hydrogen bromide (40% aq solution; 70ml) and glacial acetic acid (70ml). The reaction conditions were as described above in Step 3 for Compound 1. The product was recrystallized 25 from methanol/water (2:1). Characterizing data is provided in Table 3.

Step 3: Preparation of ethylester of (4-methylthio-4'-carboxymethoxy)benzophenone

30 The product of Step 2 (3g), potassium carbonate (3g) and ethylbromoacetate (2.8ml) were added to acetone (50ml). The reaction conditions were as described above in Step 4 for Compound 1. The product was recrystallized from ethanol. Characterizing data is provided in Table 3.

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Step 4: Preparation of (monomethylpolyethyleneglycol)<sub>350</sub> ester of (4-methylthio-4'-carboxymethoxy)benzophenone

5 The product of Step 3 (2.5g) and polyethyleneglycol monomethyl ester ( $M_n$ 350; 2.65g) were added to xylene (50ml). The reaction conditions were as described above in Step 5 for Compound 1. The final product was purified by column chromatography. Characterizing data is provided below.

10 RP-HPLC (mobile phase 50:50 acetonitrile/water, flow 1ml/min) retention time = 20.28-42.03 minutes.

FTIR 679,CS str, 1648 CO str ketone; 1756 CO str ester

15 UV-Vis: 0.001% w/v in methanol, 204.0 nm; 1.1856 abs units; 312.0 nm; 0.6835 abs units

270 MHz NMR  $^1$ H. 2.55,s,3H,-SMe; 3.375,s,3H,-CH<sub>3</sub>; 3.65,s,32H, -CH<sub>2</sub>CH<sub>2</sub>-; 4.80,s,2H,OCH<sub>2</sub>-; 6.95-7.85,AA'BB',8H, aro.

20 Compound 10: (Monomethylpolyethyleneglycol)<sub>350</sub> ether of 4-benzophenone

25 This was prepared by reacting the appropriate chloro derivative of monomethylpolyethyleneglycol - 550 with the sodium salt of 4-hydroxybenzophenone as described above for Compound 6.

30 Compound 11: Preparation of 1-(4-[Methoxy PEG<sub>3</sub>saloxypheyl])-2-hydroxy-2-methyl-propan-1-one

Step 1: Preparation of 4-Methoxy phenyl isopropyl ketone

35 Anisole (51 ml; 0.47 moles) was stirred at 5°C and aluminium chloride (40g) was added slowly and then isobutyryl chloride (25g; 0.234 moles) was added dropwise

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over 60 minutes. The reaction mixture was stirred at room temperature for 2 hours followed by heating at 60°C for 4 hours. The viscous reaction product was poured onto a mixture of ice (200 g) and concentrated HCl (100 ml). The 5 aqueous mixture was extracted with benzene and the organic fraction washed with NaOH solution (0.2M) and water and dried over anhydrous sodium sulphate. The crude brown product was purified by distillation to yield the target compound as a colourless viscous product (37.548 g; 79%).

10 The product was characterised as follows:

b.pt 72°C/0.2 mmHg

Elemental analysis: C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> %calc: C=74.13, H=7.92; % found: C=73.91; H=8.17.

NMR - δ<sub>H</sub>(270MHz; CDCl<sub>3</sub>) 1.20(6H,d,CH<sub>3</sub>), 3.50(1H,m,CH), 15 3.80(3H,s,-OMe), 6.90-7.95(4H,AA'BB', aromatic); IR-ν<sub>max</sub>/cm<sup>-1</sup> 1675(C=O str), 837(C-H def., para substituted aromatic).

Step 2: Preparation of 4-Hydroxy phenyl isopropyl ketone

20 The product of Step 1 (10g; 0.056 moles) was added to a stirred solution of HBr (40ml, 40% aq. solution) and glacial acetic acid (40ml). The solution was refluxed for 30 minutes than acetic anhydride (30ml) was added with cooling and the solution refluxed for 2 hours. The volume 25 was reduced and diluted with water (200ml) followed by extraction with dichloromethane. The organic fraction was washed with copious amounts of water and then extracted with NaOH(aq) solution (1M). The basic solution was acidified with conc. HCl and the resulting mixture 30 extracted with dichloromethane. The organic fraction was dried over sodium sulphate and the crude brown product purified by distillation to yield the target compound as an extremely viscous pale yellow liquid (5.6g; 60.7%). The product was characterised as follows:

35 b.pt 110°C C/0.3 mmHg

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Elemental analysis: C<sub>10</sub>H<sub>12</sub>O<sub>2</sub> % calc: C=73.15; H=7.37; % found: C=73.18; H=7.6.

5 NMR -  $\delta$ <sub>H</sub>(60MHz; CDCl<sub>3</sub>) 1.25(6H,d,CH<sub>3</sub>), 3.60(1H,m,CH), 7.00-8.15(4H,AA'BB',aromatic), 8.30(1H,s,-OH); IR-  $\nu$ <sub>max</sub>/cm<sup>-1</sup> 3288(-OH str), 1658(C=O str), 844(C-H def., para substituted aromatic).

Step 3: Preparation of acetate ester of 1-(4-hydroxy phenyl)2-hydroxy-2-methyl-propan-1-one

10 The product of Step 2 (3.5g; 0.021 moles) was added to acetic anhydride (125 ml) and refluxed for 10 hours. Acetic anhydride was removed under vacuum and the residue added to dichloromethane. The organic solution was washed with water and sodium bicarbonate solution before drying over sodium sulphate. The crude product was purified by distillation to yield the target compound as a colourless liquid (3.6g, 83%). The product was characterised as follows:

20 bpt 82°C/0.225 mmHg.

Elemental analysis: C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>. % calc: C=69.88; H = 6.84; % found C=69.97; H=6.98.  
NMR  $\delta$ <sub>H</sub>(100MHz; CDCl<sub>3</sub>) 1.20(6H,d,CH<sub>3</sub>), 2.275(3H,s,acetate -CH<sub>3</sub>), 3.475(1H,m,CH), 7.00-8.05(4H,AA'BB',aromatic); IR- $\nu$ <sub>max</sub>/cm<sup>-1</sup> 1765(acetate C=O str), 1682(ketone C=O str), 844(C-H def., para substituted aromatic).

Step 4: Preparation of acetate ester of 1-(4-hydroxy phenyl) -2-bromo-2-methyl-propan-1-one

30 The product of Step 3 (25g; 0.12 moles) was added to glacial acetic acid (35ml). A solution of bromine (7.8ml; 0.15 moles) in glacial acetic acid (20ml) solution was dropped onto the solution which was stirred at room temperature for 12 hours. The reaction solution was added to ice (200g) and the resulting mixture extracted with

- 25 -

ethyl acetate. The organic fraction was washed with water and dried over sodium sulphate. Removal of solvent yielded the target compound as a straw coloured liquid, that was used without further purification.

5        NMR -  $\delta$ <sub>H</sub> (100MHz; CDCl<sub>3</sub>) 2.05 (6H, s, CH<sub>3</sub>), 2.35 (3H, s, acetate-CH<sub>3</sub>), 7.20-8.50 (4H, AA'BB', aromatic).

Step 5: Preparation of 1-[4-hydroxyphenyl]2-hydroxy-2-methyl-propan-1-one

10       The product of Step 4 (32g) was added to ethanol (120ml) and cooled to 5°C. NaOH<sub>(aq)</sub> solution (40ml; 1M) was dropped on to the ethanol solution over 20 minutes. The reaction solution was stirred at 10°C for 30 minutes and room temperature for 60 minutes then diluted with water (70ml). The aqueous solution was acidified to ~ pH 5 with 5M HCl<sub>(aq)</sub> and extracted with ethyl acetate. The organic fraction was dried over sodium sulphate. Removal of solvent yielded the target compound as a white solid (10.1g, 46.7%).

20

The product was characterised as follows:

mpt 124-126°C (from 1:1 acetone/pet.ether bpt 40-60)

Elemental analysis: C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>. %calc: C=66.65; H=6.71; %found: C=65.97; H=7.09.

25       NMR -  $\delta$ <sub>H</sub> (270MHz; CDCl<sub>3</sub>) 1.60 (6H, s, CH<sub>3</sub>), 4.70 (1H, s, tertiary -OH), 6.80-8.30 (4H, AA'BB', aromatic); 9.10 (1H, s, phenolic -OH; IR- $\nu$ <sub>max/cm<sup>-1</sup></sub> 3428 (free OH str), 3157 (OH str), 1650 (C=O str); RP-HPLC ( $\lambda$ 254nm, 70:30 acetonitrile/water mobile phase, C18 analytical column, 1ml/min flow rate) retention time 3.30 minutes;  $\lambda$ <sub>max</sub>(MeOH)/nm 203.2 ( $\epsilon$ /dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> 10200), 220.8 (9260), 279.2 (13200).

Step 6: Preparation of title compound

35       The product of Step 5 (3g; 0.0167 moles), potassium carbonate (5g) and either 7.25g of the tosylate ester of

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5 polyethylene glycol<sub>350</sub> monomethylether or 6g of the chloro-derivative of polyethylene glycol<sub>350</sub> monomethylether, were refluxed in acetone (50ml) for 18 hours. The inorganic salts were filtered and the crude product was purified by column chromatography(200-400 mesh silica gel,2:1 ethyl acetate/pet ether bp. 40-60°C) to yield the target compound as a viscous liquid.

10 NMR -  $\delta$ <sub>H</sub>(270MHz; CDCl<sub>3</sub>) 1.60(6H,s,CH<sub>3</sub>), 3.35(3H,s,-OMe), 3.60(28H,s,-CH<sub>2</sub>CH<sub>2</sub>), 6.90-8.10(4H,AA'BB',aro.);  
RP-HPLC ( $\lambda$ 254nm, 50:50 acetonitrile/water mobile phase, C18 analytical column, 1ml/min flow rate) retention time 6.31-12.80 minutes;  $\lambda_{max}$  (MeOH)/nm 203.2(1.67 abs. Units 0.001% w/v), 221.6(0.72), 274.4(0.40).

15

Compounds 12, 13 and 14

These were prepared by processes analogous to processes described above.

20

Compound C1: Diethyl-4',-di(carboxymethoxy)benzophenone

25 This was the product of Step 1 in the preparation of compound 1 above.

Compound C2: A mixture comprising ethyl-2-(carboxymethoxy)thioxanthone and ethyl-4-(carboxymethoxy)thioxanthone.

30

This was the product of Step 1 in the preparation of compound 3 above.

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Compound C3: a mixture comprising 2- and 4-isopropylthioxanthone (ITX), a commercially available photoinitiator.

5           Compound C4

This was prepared as described in the applicant's co-pending application number PCT/GB96/00911 and was referred to therein as compound 2.

10           Compound C5

This is a compound of the type referred to in Japanese published patent application 6263814 (Toyo Ink) and described in the applicant's co-pending application number PCT/GB96/00911 as compound C1.

15

Compound C6

This was the product of Step 1 in the preparation of Compound 4.

20           Compound C7

This was commercially available from Ciba-Geigy.

Compound C8

This was commercially available.

25

Compound C9

This was prepared by processes analogous to those described above.

30           Compound C10

This was prepared by a process analogous to those for Compounds 12 to 14.

Effectiveness of compounds as curing agents

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For the purpose of these tests, unless otherwise stated, the standard pre-polymer mixture was as follows:

5        1-6 hexanediol Diacrylate (monomer) : 93 wt%  
          amine curing agent : 5 wt%  
          photoinitiator : 2 wt%

10        It was found that all of the compounds and the comparison compounds dissolved into the prepolymer mixtures.

15        Curing was by a medium pressure UV lamp. The results presented below relate to the determination of whether the polymer cures and if so, how quickly, and to the propensity of the photoinitiators to migrate from a polymer film after curing. In general, the two methods employed to address these aspects were Reflectance FTIR analysis and High Pressure Liquid Chromatography (HPLC).  
20        For examples 7 and C9, the extent of reaction was determined by transmittance FTIR as shown in figure 11.

#### Methods of Data Acquisition

##### Method 1

25        Reflectance FTIR analysis of degree of cure achieved.

The degree of cure in films, exposed to UV light, was determined as follows:

30        Compounds were spread to a thickness of 12  $\mu\text{m}$  on polished aluminium slides then exposed to UV light in a Colordry unit. Infrared spectra of the films were run using a Digilab FTIR spectrometer (FTS60) equipped with a microscope (uMA 300A). The latter was used in the reflectance mode. By measuring the intensity of the  $810 \text{ cm}^{-1}$

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band (associated with the acrylate group) the extent to which cure had occurred could be determined.

Method 2

5 HPLC method used for analysing the propensity of the initiators to migrate

The method for testing the propensity of the initiators to migrate was the same throughout.

10 The migratable initiator content of each film was analysed as follows. Initially a drop of the pre-polymer mixture was placed on a piece of satinised paper. This was then evenly spread over the surface using a "K" bar which gave a film thickness of between 50-60  $\mu\text{m}$ .

15

For each of the initiators samples of film were taken after various passes of the Colordry unit (i.e., the UV lamp), as shown below in the figures.

20 The Colordry unit contains a fusion lamp system (a hydrogen bulb electrode-less lamp). The samples are placed on a moving belt (in these trials this was set at 45 metres/minute). It was important to ensure that all the samples taken, of satinised paper and film, were of the same size. It was for this reason that a metal template was made that gave samples of 25 x 60 mm. In addition, for most examples, steps were taken to ensure that the curing of the film was as unaffected by oxygen inhibition as possible. This was ensured by placing the paper and uncured film in a cell with a quartz window. This cell was then evacuated with nitrogen and sealed. Only then was the sample passed through the Colordry unit. The only examples wherein polymerisation was carried out in air were those shown in figures 8, 9, 13 and 4.

35

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The 25 x 60 mm samples of each pre-polymer mixture were then placed in individual 7 ml sample vials. To each vial was added 5 ml of a de-gassed acetonitrile/water 50/50 mix, enough to immerse each sample. The vials were 5 then placed in a dark cupboard for 20 hours. After this time the vials were removed and the sample extracted from each vial. All that was left in each vial was the solvent containing the migratables that had leached out from the film in the 20 hour period.

10

The samples were then prepared for HPLC analysis by filtering each one using Sartorus Millistart 0.45  $\mu$ m disposable filters. This was to ensure that there were no solid contaminants that would damage the HPLC column.

15

Chromatographs of the initiator components for each of the films were run prior to the trials. This was to ensure that firstly the elution time was known and, secondly, to determine whether the respective initiator 20 components had any characteristic shaped peaks.

25 After filtration each sample was injected on to the HPLC column. Each sample was run in acetonitrile/water 50/50 mixture. The data from each run was then used to analyse the migratable content of each film.

On the chromatogram for the solution containing 30 migrated initiator compound, the area under each of the relevant peaks was noted.

35

It was assumed that the contents of the solution that had contained the film that had not passed the UV lamp, contained 100% migratable initiator compound, because the pre-polymer mixture was not irradiated. The values for 35 the areas under the peaks from the solutions that had

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contained films that had passed the UV lamp could then be correlated respectively to the 100% migration value of the uncured solution.

5        Results of the assessments described in Methods 1 and 2 above are provided in the figures, wherein the table below lists the examples of the invention and/or the comparative examples represented in the figures.

10	Figure No.	Assessment made	Examples of invention shown	Comparative examples
	1	% migration	1, 2	C1
	2	degree of cure	3	C2, C3
	3	% migration	3	C2, C3
	4	degree of cure	3, 4, 5	C3, C6
15	5	% migration	3, 4, 5	C3, C6
	6	degree of cure	8, 9	-
	7	% migration	8, 9	-
	8	degree of cure	11	C7, C8
	9	% migration	11	C7, C8
20	10	degree of cure	6	-
	11	extent of reaction	7	C9

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12	degree of migration	7	C9
13	degree of cure	12,13,14	C10
14	degree of migration	12,13,14	C10

5 In addition, Table 1 below reproduces part of Table 1 in the applicant's co-pending application number PCT/GB96/00911 in order to compare % migration of compounds C4 and C5 (compounds 2 and C1 in PCT/GB96/00911). The compounds referred to in the table 10 were components of a composition comprising: 1,6-hexanediol diacrylate(monomer) (93wt%); amine curing agent, N-methyldiethanolamine (5wt%); and photoinitiator (2wt%).

15 Table 1  
Percentage migration of initiator after stated number  
of passes under UV source

No. of passes of UV source	Compound C4	Compound C5
0	100	100
2	86.12	62.1
4	57.07	53.37
8	32.87	51.07

25 It will be noted from Table 1 that compound C4 had significantly less migration than compound C5 after 8 passes of the source. It will also be noted from figure 1 that compound C4 and compound 2 have similar low % migration and, in view of this, one expects the %

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migration of compounds of the present invention to be less than those described in Japanese published patent application 6263814 (Toyo Ink) referred to above.

5       Applicant has also shown that compounds 1 to 3 are as effective initiators as compounds C3 and C4 (weight for weight). This is surprising since compounds containing a PEG moiety have significantly greater molecular weights compared to, for example, compounds C1, C2, C3 and, 10 therefore, the molar ratio of compounds 1 to 3 used is significantly less than that for C1, C2 and C3.

15       The results show, in general, that compounds that incorporate a PEG moiety into an aliphatic side chain exhibit relatively low % migration and/or odour compared to analogous compounds which do not include PEG. Such compounds can, therefore, be used advantageously in applications where low migration properties are desired, for example, for packing materials for foodstuffs.

20       The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

30       All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

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Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly 5 stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

10 The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any 15 novel one, or any novel combination, of the steps of any method or process so disclosed.

Table 2 (Re: Compound 8)

Product of Step No.	IR Spectrum (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)	Elemental Analysis		Melting Point (°C)	Relative Molecular Mass	Molecular Formula
			Calc	Found			
1	850, C-H def (aro.) 1251, C=O str (ether) 1635, C=O str	3.80, s, 3H, -OMe; 6.80-7.80, m, 8H, aro	C=68.16 H=4.49	C=67.89 H=4.24	121-122	246.692	C <sub>14</sub> H <sub>11</sub> ClO <sub>2</sub>
2	679.8, C-S str	3.95, s, 3H, -OMe; 6.99-8.025, m, 13H, aro	C=74.97 H=5.03	C=74.97 H=5.19	78-80	320.408	C <sub>10</sub> H <sub>16</sub> O <sub>2</sub> S
3	683, C-S str 1637, C=O str, ketone 3292, O-H str	6.80-7.70, m, aro.	C=74.49 H=4.61	C=74.34 H=4.46	149-151	306.381	C <sub>19</sub> H <sub>14</sub> O <sub>2</sub> S
4	679, C-S str 1643, C=O str, ketone 1763, C-O str, ester	1.30, t, 3H, -Me; 4.25, q, 2H, CO <sub>2</sub> CH <sub>2</sub> ;-; 4.60, s, 2H, -OCH <sub>2</sub> CO <sub>2</sub> -; 6.90-7.80, m, 13H, aro	C=70.39 H=5.14	C=70.18 H=5.10	58-59	392.473	C <sub>21</sub> H <sub>20</sub> O <sub>4</sub> S

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Product of Step No.	IR Spectrum (cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)	Elemental Analysis		Melting Point (°C)	Relative Molecular Mass	Molecular Formula
			Calc	Found			
5	690, C-S str 1650, C-Ostr, ketone 1759, C-Ostr, ester	3.38, s, 3H, -OMe; 3.65, s, 2H, -CH <sub>2</sub> CH <sub>2</sub> -; 4.85, s, 2H, -OCH <sub>2</sub> CO <sub>2</sub> -; 6.93-7.83, m, 13H, aro.					

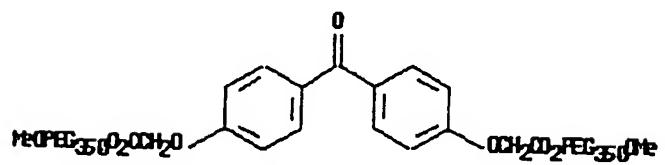
Table 3 (Re: Compound 2)

Product of Step No.	IR Spectrum (Cm <sup>-1</sup> )	<sup>1</sup> H NMR (δ ppm)	Elemental Analysis		Melting Point (°C)	Relative Molecular Mass	Molecular Formula
			Calc	Found			
1	679, C-Sstr 1648, C=Ostr 1640, C=Ostr 3303, O-Hstr	2.60, s, 3H, -SMe, 3.90, s, 3H, -OMe; 6.90-8.00, m, 8H, aro.	C=69.74 H=5.46	C=69.61 H=5.25	118-119	258.337	C <sub>13</sub> H <sub>14</sub> O <sub>2</sub> S
2	679, C-Sstr 1640, C=Ostr 3303, O-Hstr	2.55, s, 3H, -SMe; 6.85-7.75, m, 8H, aro.	C=68.83 H=4.95	C=68.71 H=4.80	136-137	244.31	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> S
3	679, C-Sstr 1637, C=Ostr, ketone 1760, C=Ostr, ester	1.30, t, 3H, -Me; 2.53, s, 3H, -SMe; 4.25, q, 2H, CO <sub>2</sub> CH <sub>2</sub> -; 4.65, s, 2H, -OCH <sub>2</sub> CO <sub>2</sub> -; 6.95-7.90, m, 8H, aro.	C=65.43 H=5.49	C=65.11 H=5.56	93-95	330.402	C <sub>18</sub> H <sub>18</sub> O <sub>4</sub> S

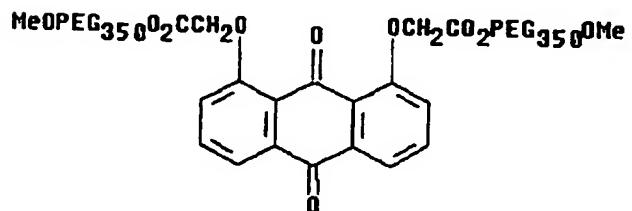
- 38 -

SUMMARY OF COMPOUNDS

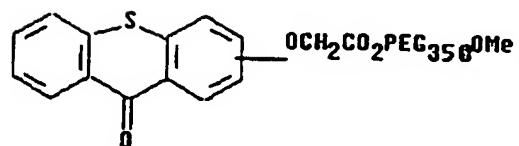
Compound 1



Compound 2

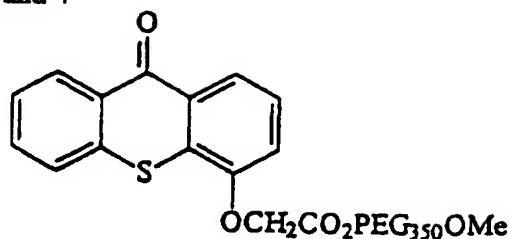


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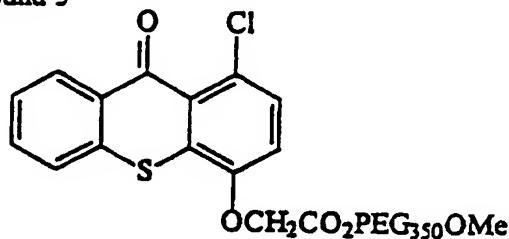


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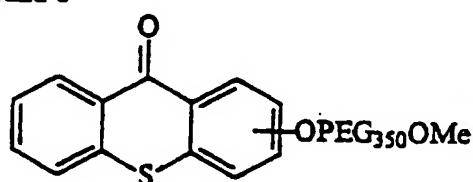
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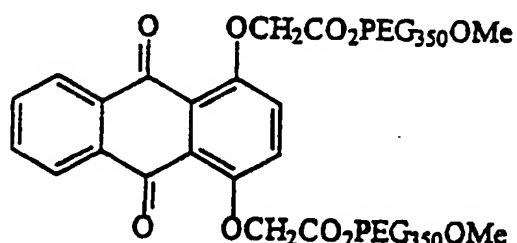
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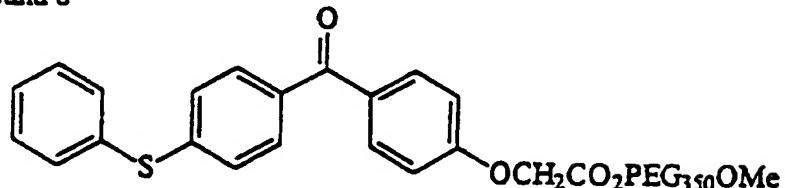
Compound 6



Compound 7

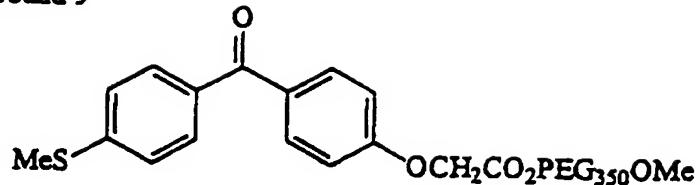


Compound 8

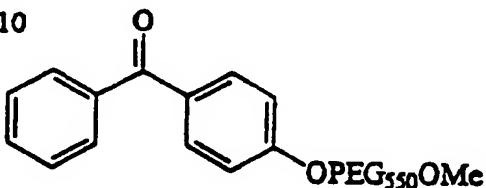


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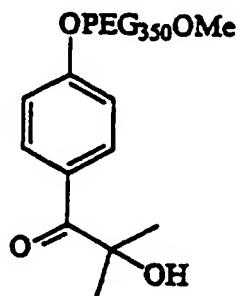
Compound 9



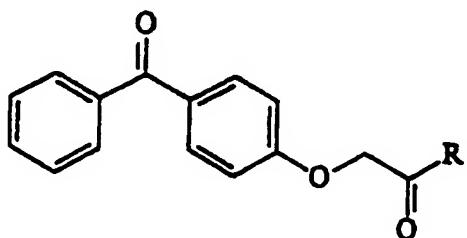
Compound 10



Compound 11

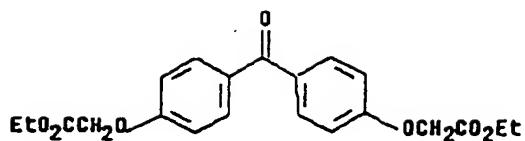


Compounds 12, 13, 14

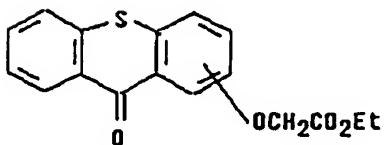
Compound 12 R= OPEG<sub>350</sub>OMeCompound 13 R= OPEG<sub>550</sub>OMeCompound 14 R= OPEG<sub>750</sub>OMe

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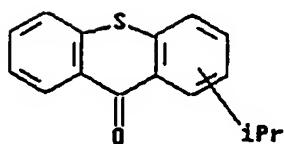
Compound C1



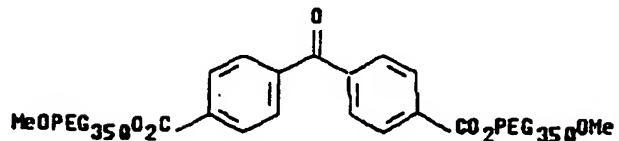
Compound C2



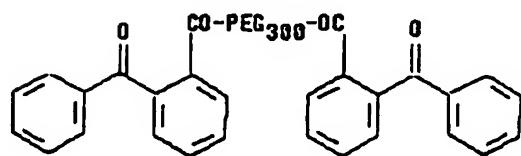
Compound C3



Compound C4

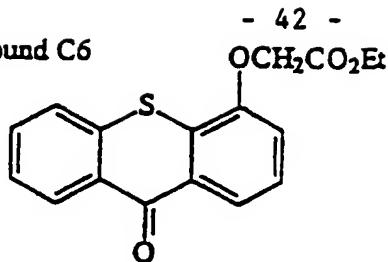


Compound C5

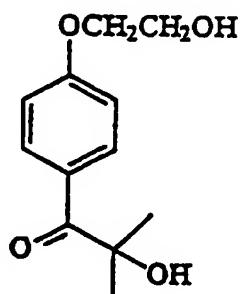


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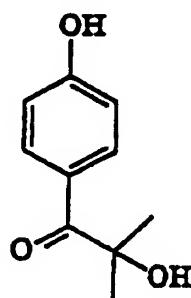
### Compound C6



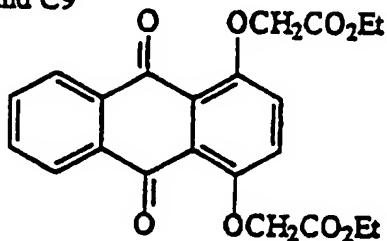
### Compound C7



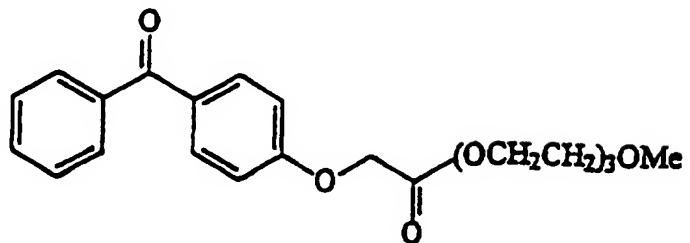
### Compound C8



## Compound C9



### Compound C10



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CLAIMS

1. A compound for use as a photoinitiator, comprising a photoreactive portion and a pendent group, said photoreactive portion including an aromatic moiety and said pendent group incorporating at least one optionally-substituted poly(alkylene glycol) moiety.

2. A compound according to Claim 1, wherein said optionally substituted poly(alkylene glycol) moiety is of general formula



wherein  $\text{R}^1$  represents an optionally substituted alkyl group,  $\text{R}^3$  and  $\text{R}^5$  independently represent a hydrogen atom or an optionally substituted alkyl group and  $x$  represents an integer.

3. A compound according to Claim 2, wherein  $\text{R}^3$  represents a hydrogen atom or an alkyl group and  $\text{R}^5$  represents a hydrogen atom.

4. A compound according to Claim 2 or Claim 3, wherein  $x$  has a mean value of greater than 3 and less than 20.

25 5. A compound according to any preceding claim, wherein said optionally-substituted poly(alkylene glycol) moiety has an average molecular weight (excluding any optional substituents) of at least 150 and less than 900.

30 6. A compound according to any of Claims 2 to 5, wherein said moiety of general formula I is linked directly to said photoreactive portion via the ether-oxygen atom thereof or is linked thereto by a linking group arranged

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between said photoreactive portion and said moiety of formula I.

5 7. A compound according to Claim 6, wherein said linking group includes either: a first moiety of general formula - CR<sup>2</sup>,CO- wherein groups R<sup>2</sup> independently represent a hydrogen atom or an alkyl group; or a group -CO-; optionally with an intermediate moiety being arranged between said photoreactive portion and said first moiety or group -CO-.

10

8. A compound according to any preceding claim, wherein the or each pendent group is an aliphatic group.

15 9. A compound according to any preceding claim, wherein said photoreactive portion incorporates an optionally-substituted phenylcarbonyl moiety.

20 10. A compound according to any preceding claim, wherein said photoreactive portion is selected from optionally-substituted benzaldehyde, benzophenone, anthraquinone, thioxanthone, thiophenylbenzophenone (especially 4-(thiophenyl)benzophenone) and benzoin derivatives.

25 11. A process for the preparation of a compound according to any preceding claim, the process comprising:

30 (a) (i) reacting a compound corresponding to said photoreactive portion but including one or more active atoms or groups with a precursor of said pendent group so that said precursor replaces said active atom or group; and

(ii) optionally derivatising said precursor of said pendent group; or

35

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(b)(i) reacting a compound which includes a moiety corresponding to a first portion of said photoreactive portion but including an active atom or group, with a precursor of said pendent group so that said precursor  
5 replaces said active atom or group;

(ii) reacting the product of step (b)(i) with a moiety corresponding to a second portion of said photoreactive portion; and  
10

iii) optionally derivatising said precursor of said pendent group.

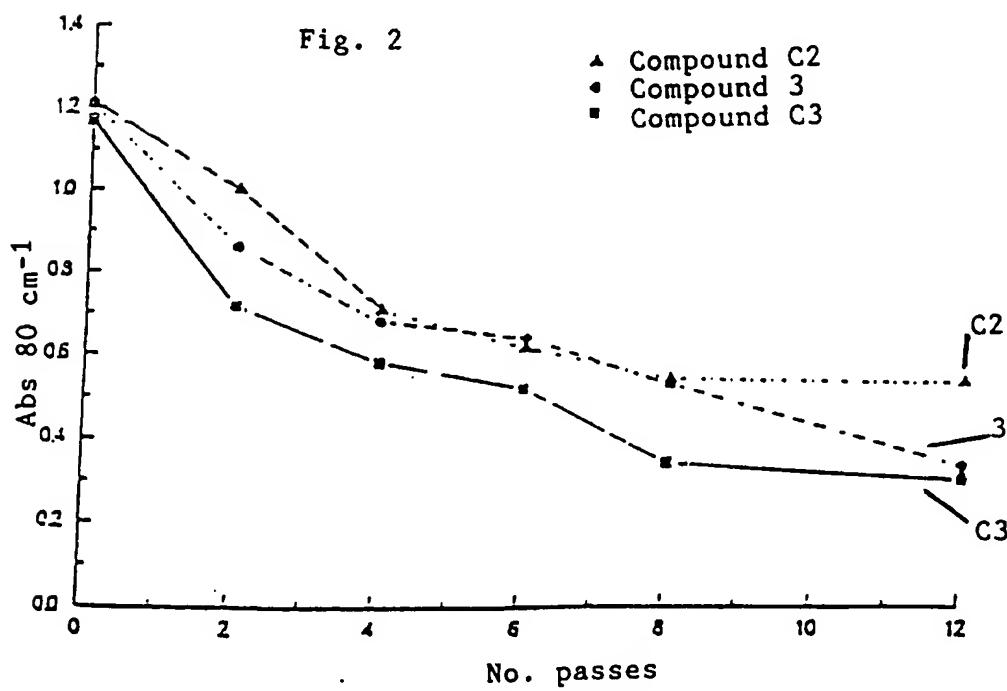
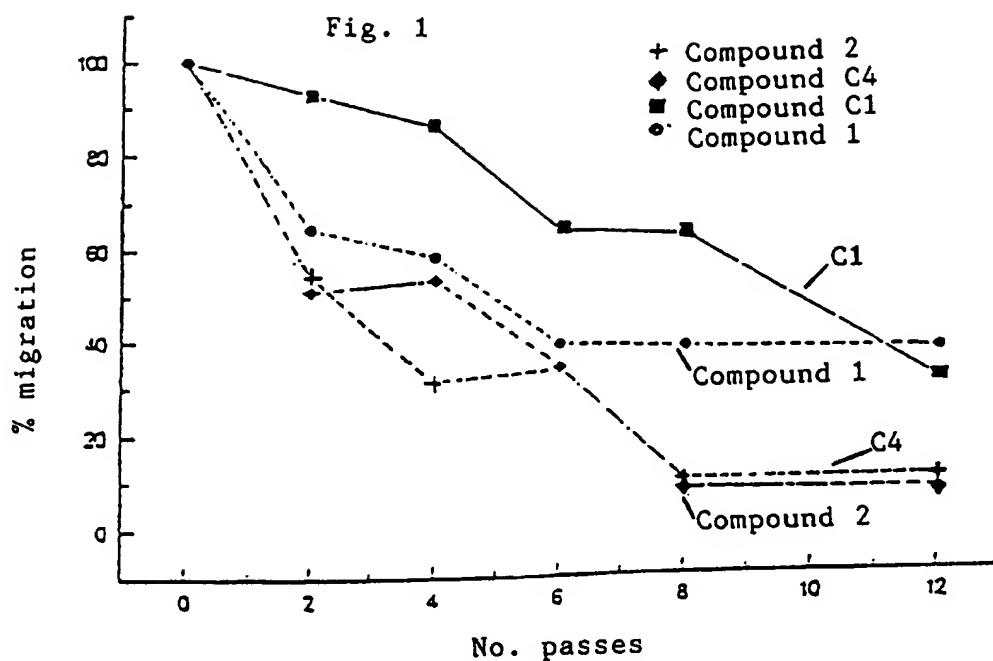
12. Use of a compound according to any of Claims 1 to 10  
15 in a polymerisation reaction.

13. A polymer curing composition comprising a compound according to any of Claims 1 to 10 together with a curing agent with which the compound may react, when irradiated,  
20 to generate a polymerisation specie.

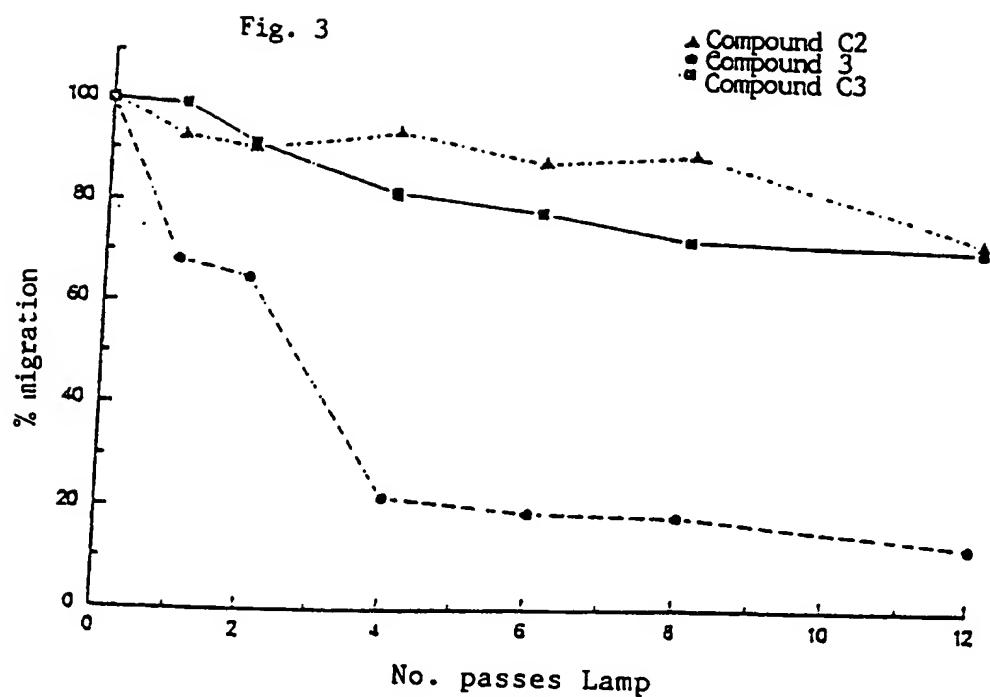
14. A polymerisable composition comprising a polymerisable material and a compound according to any of Claims 1 to 10.

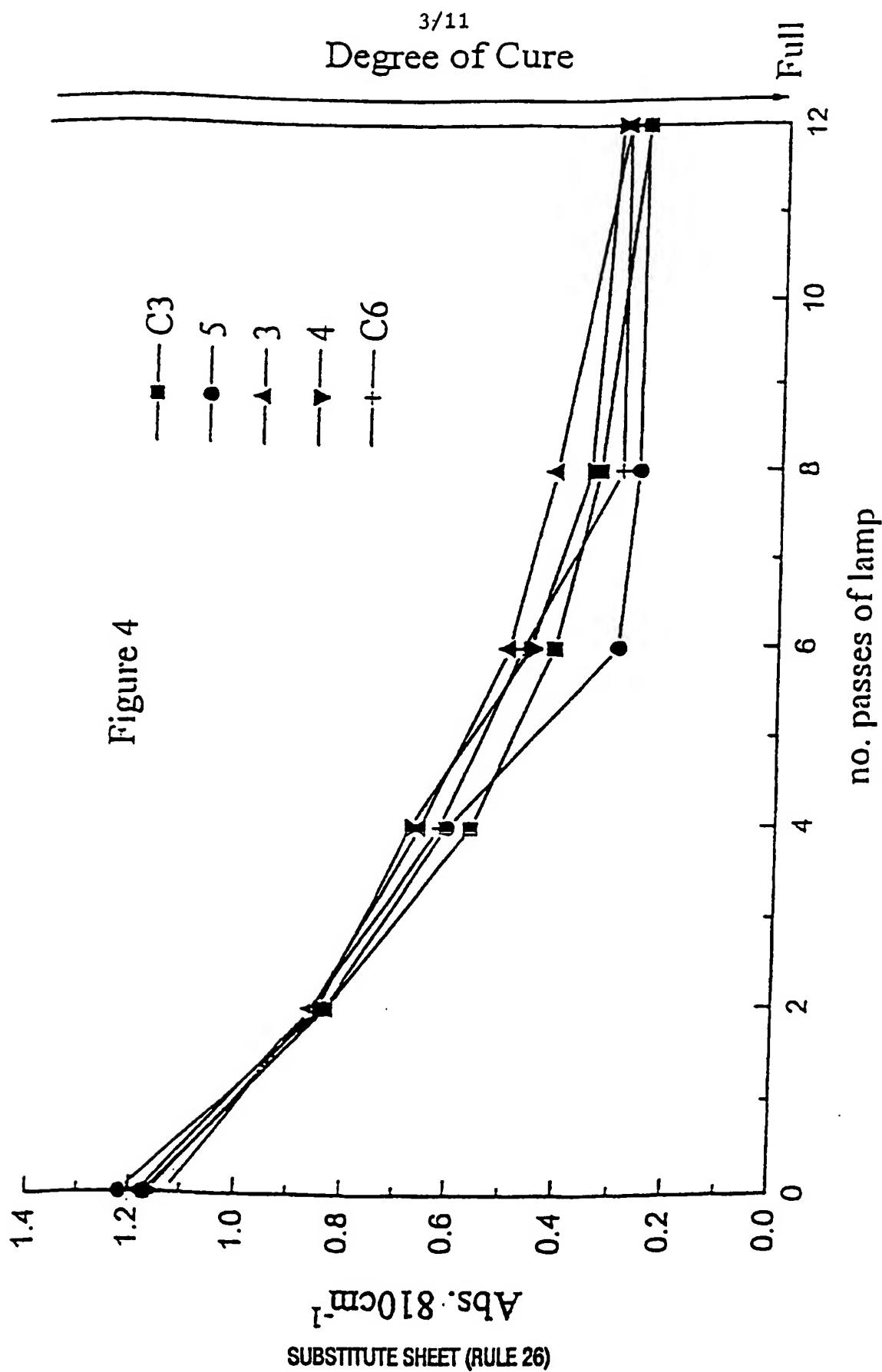
25 15. A polymeric composition prepared using a compound according to any of Claims 1 to 10 by photocuring.

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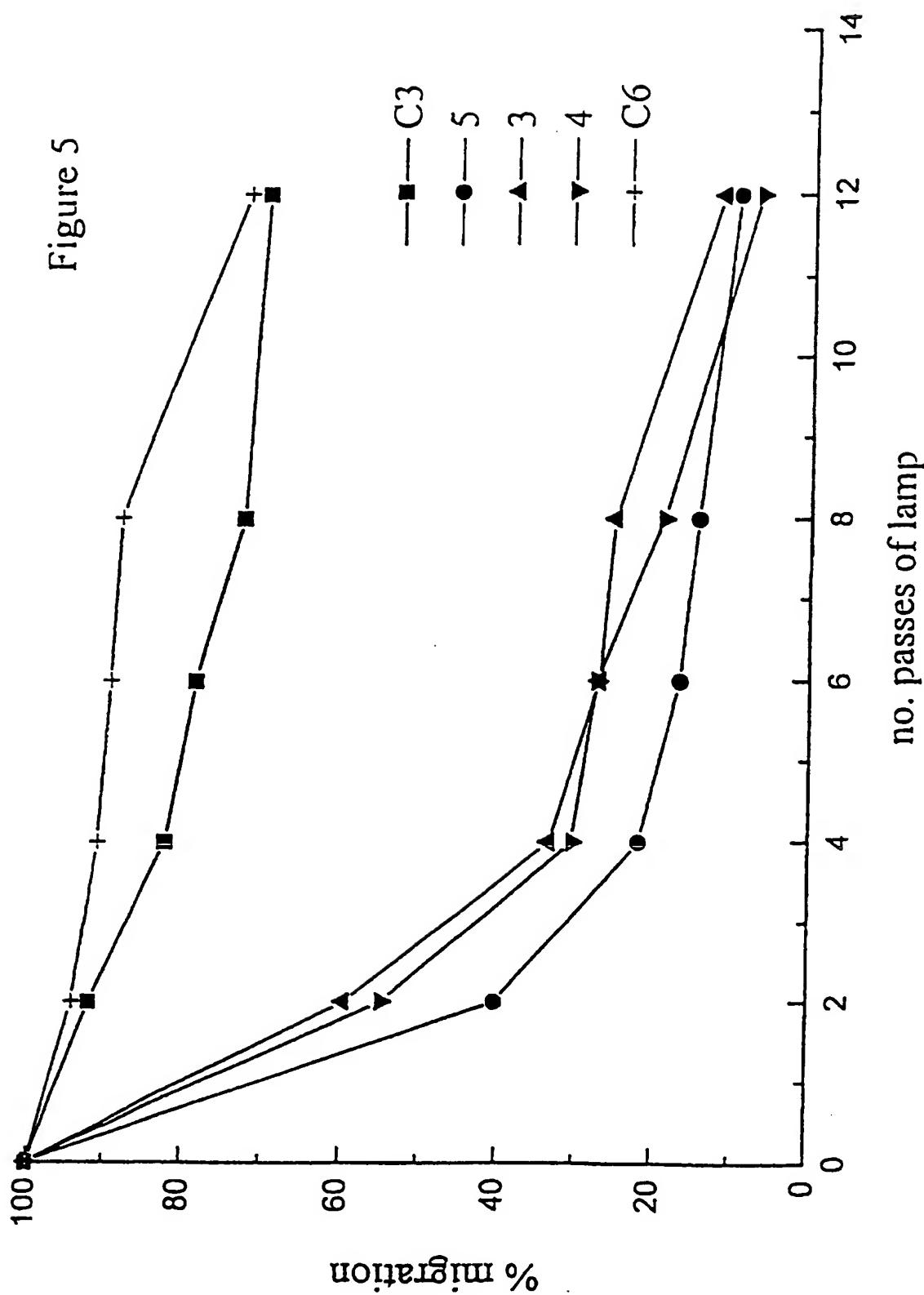
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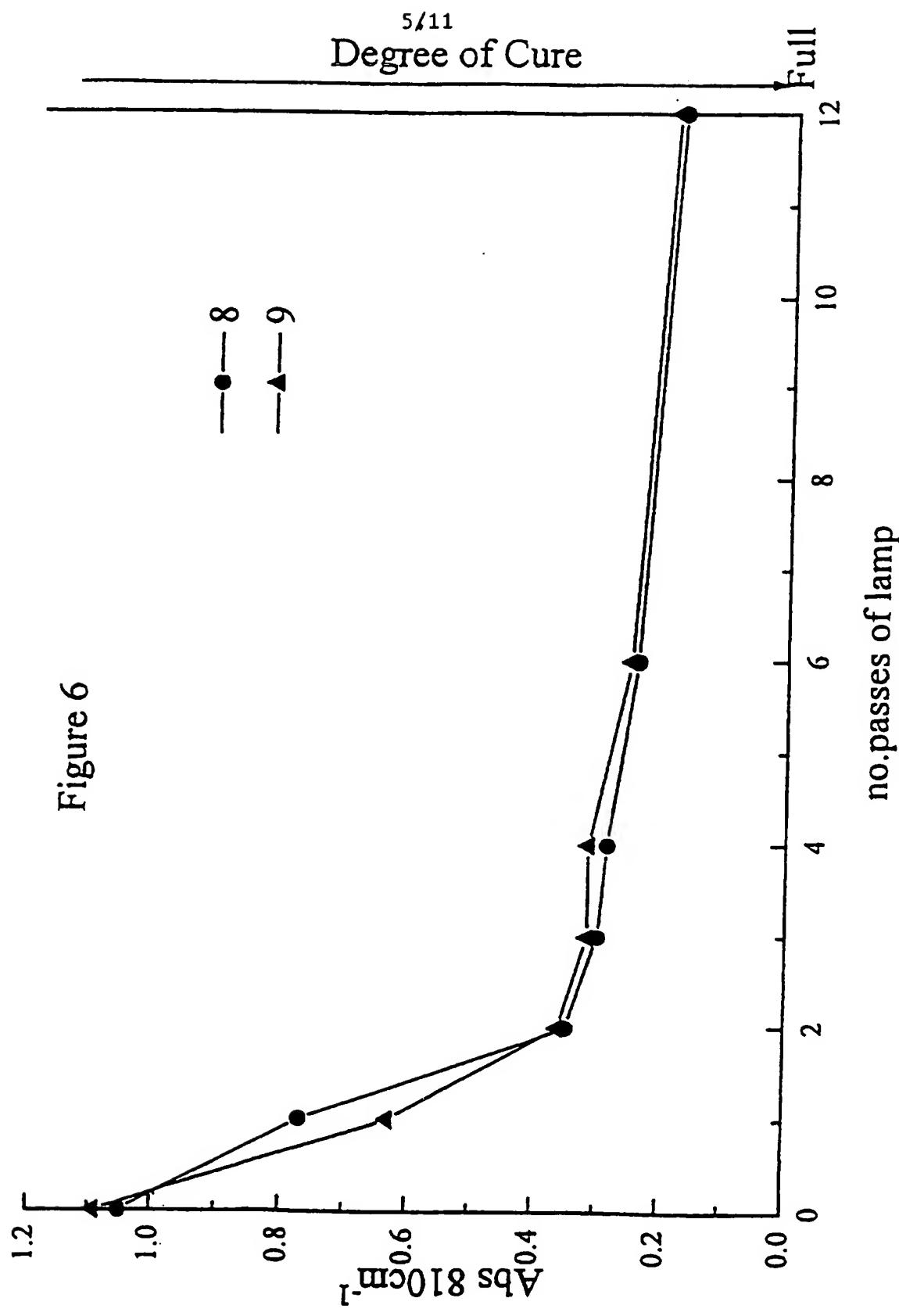




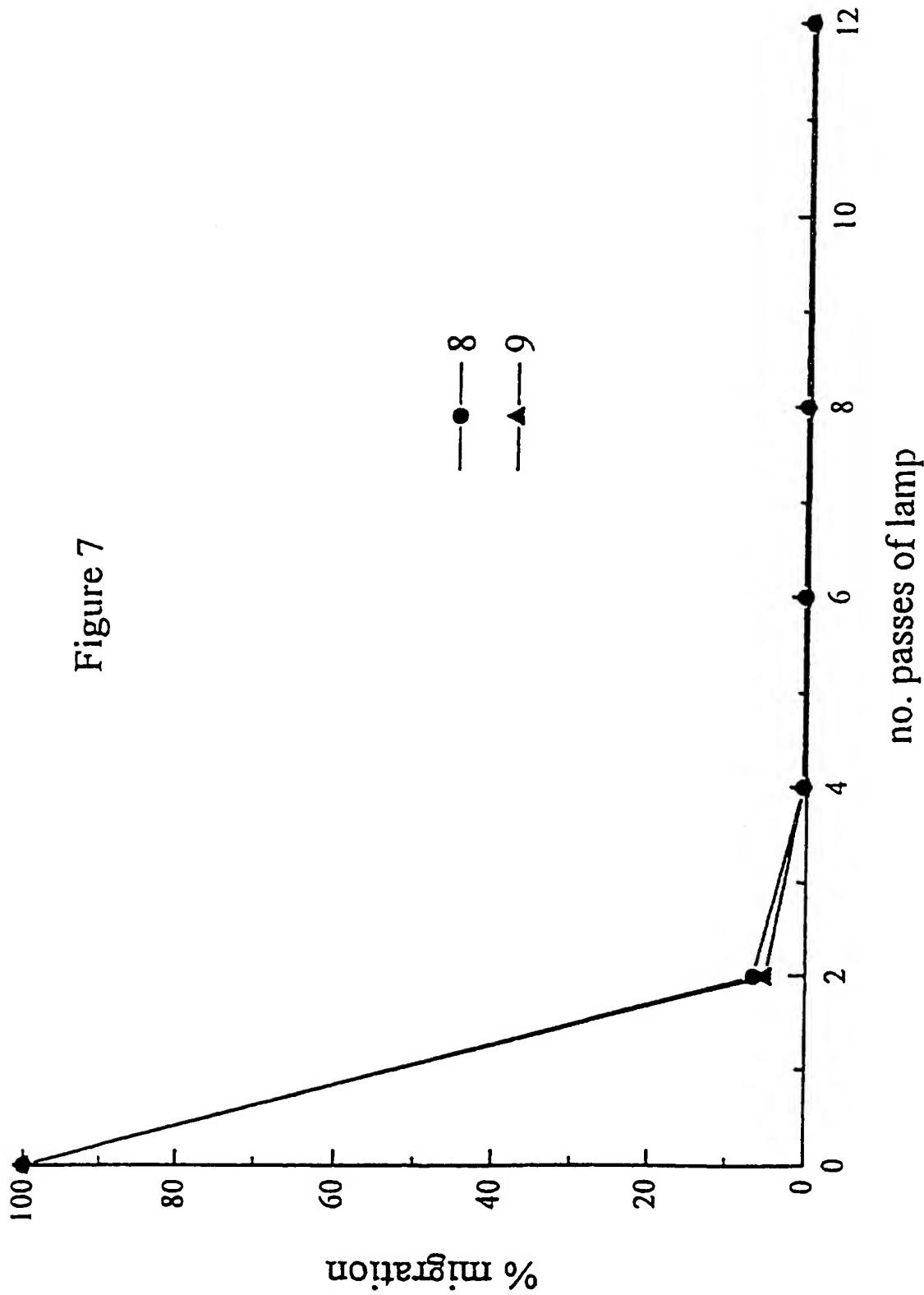
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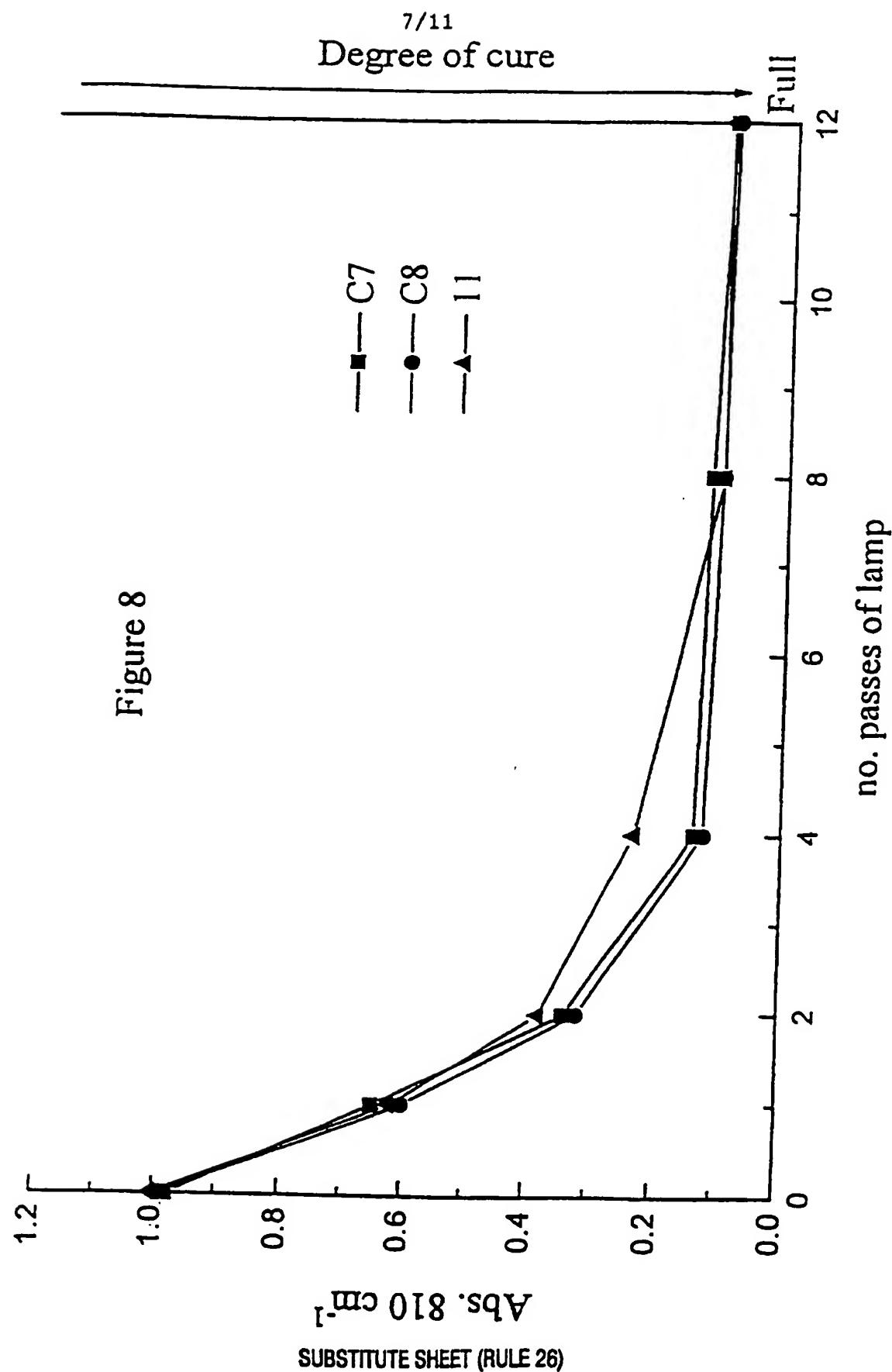
Figure 5

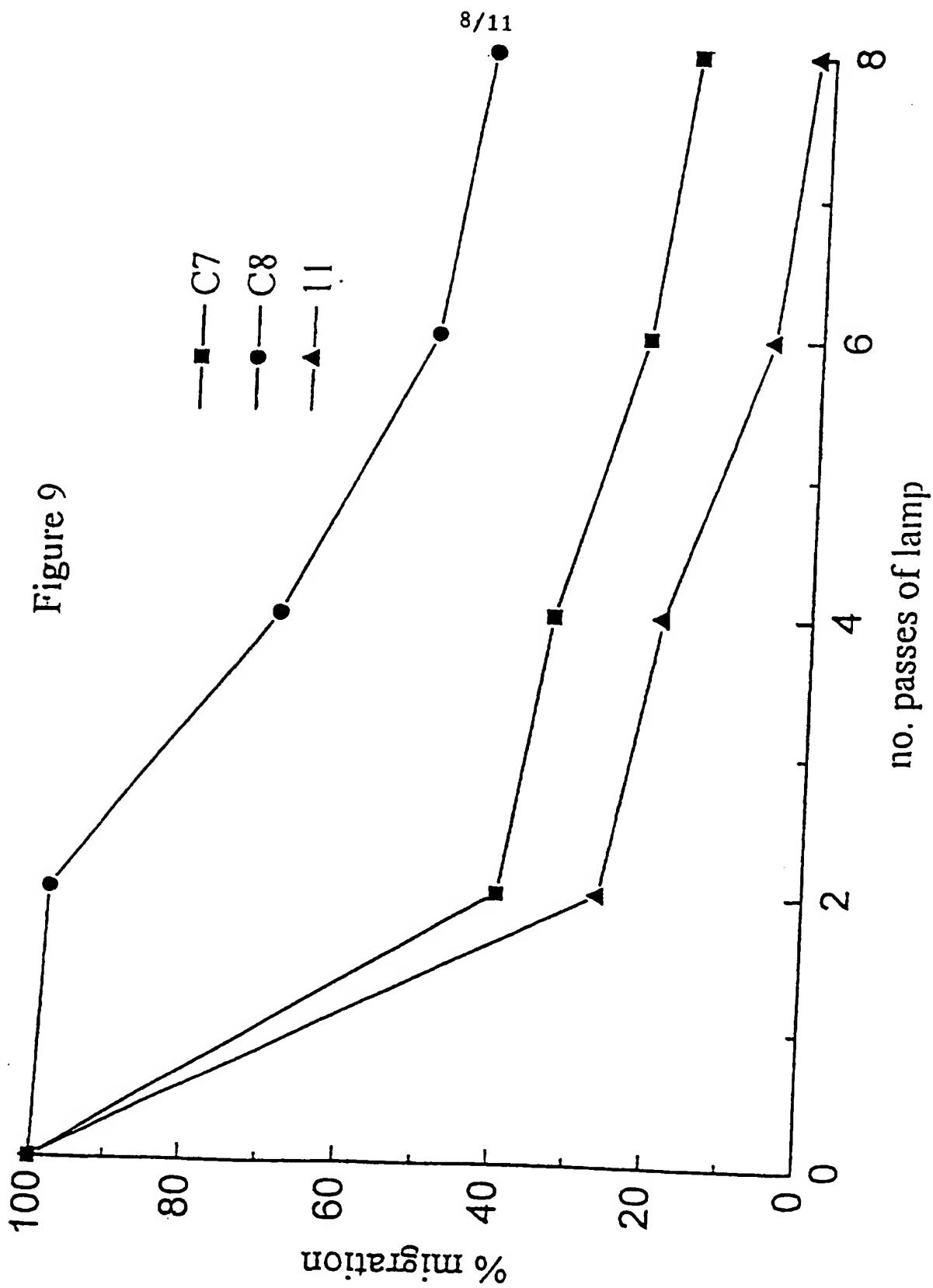




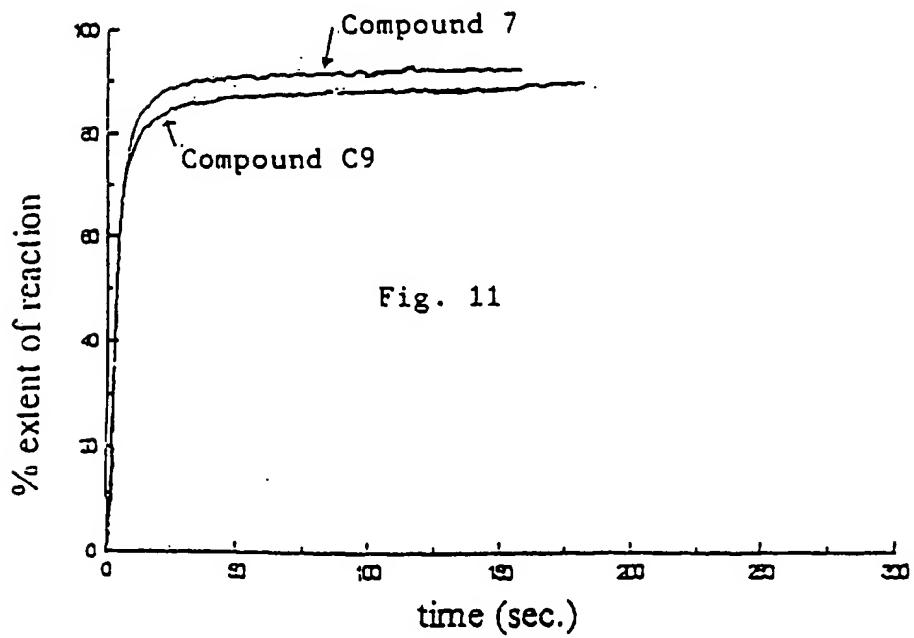
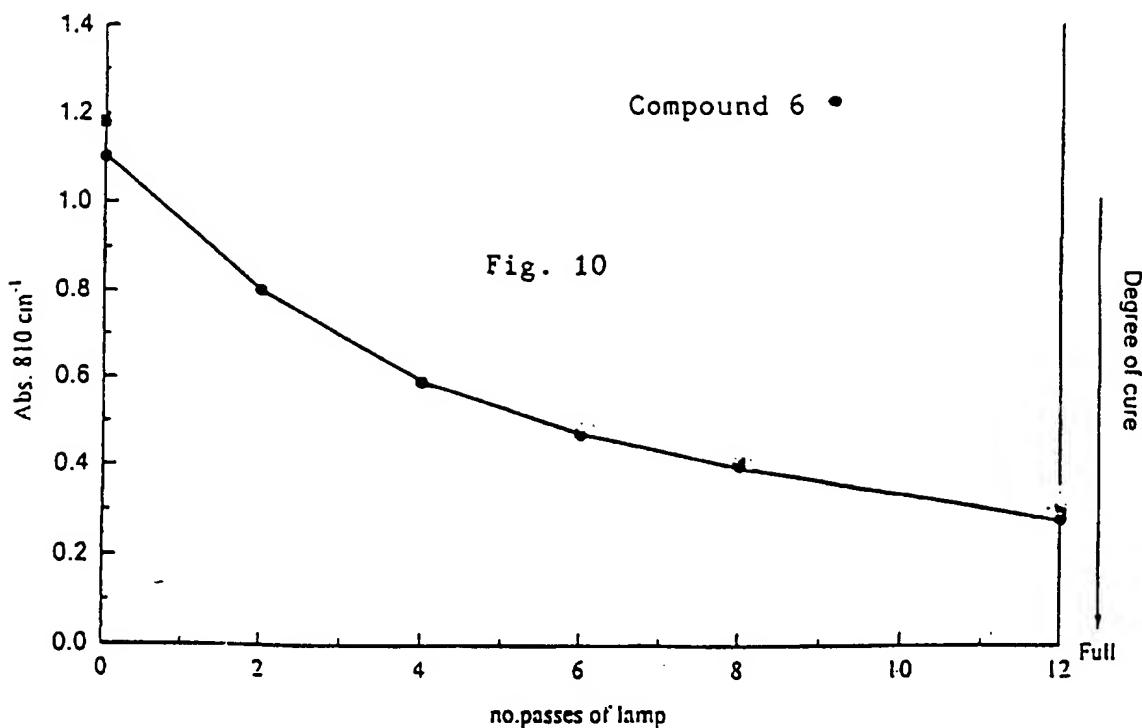
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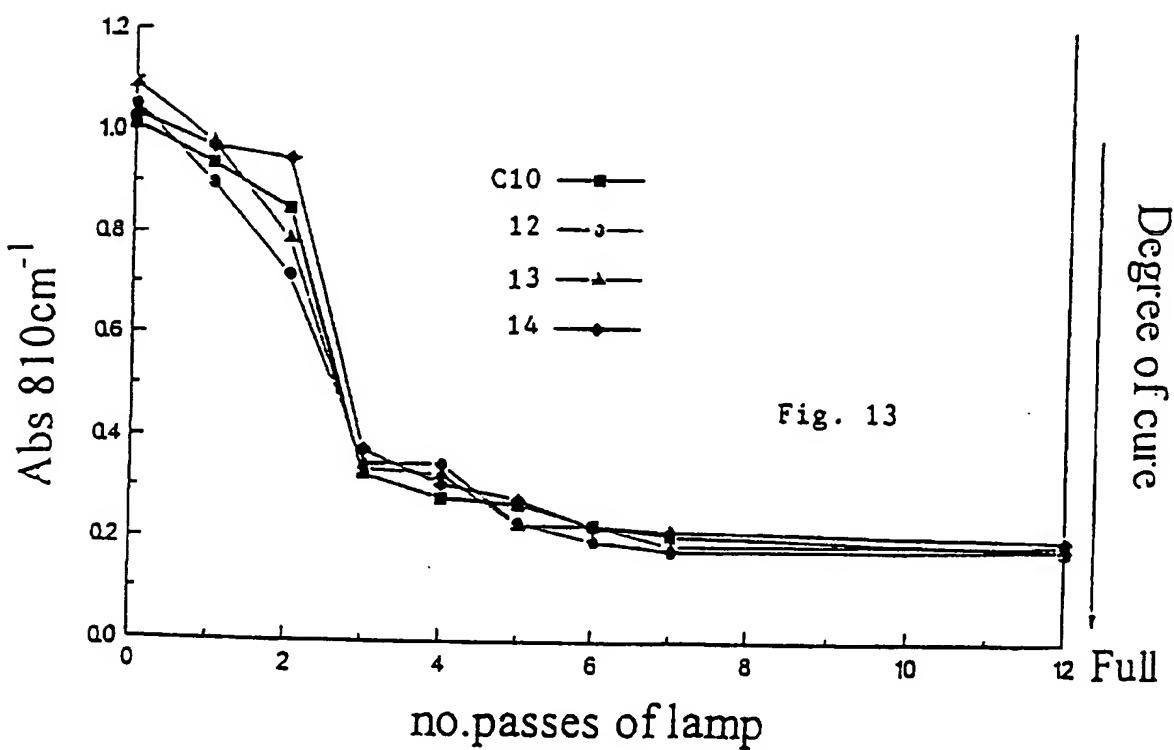
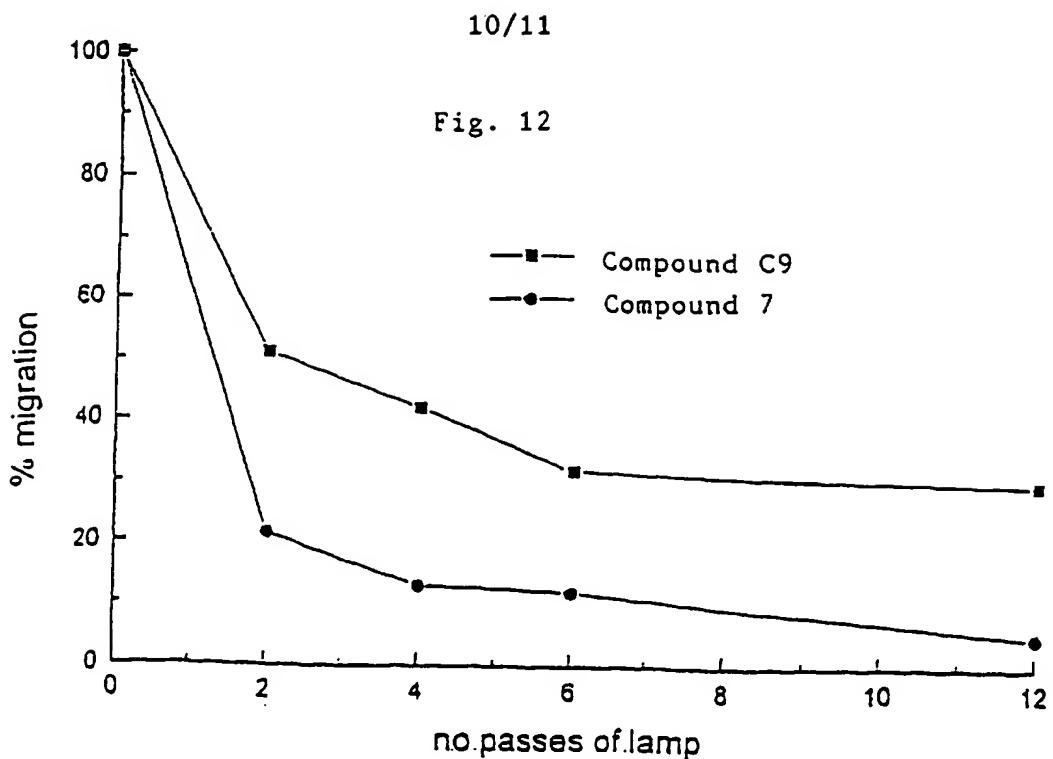




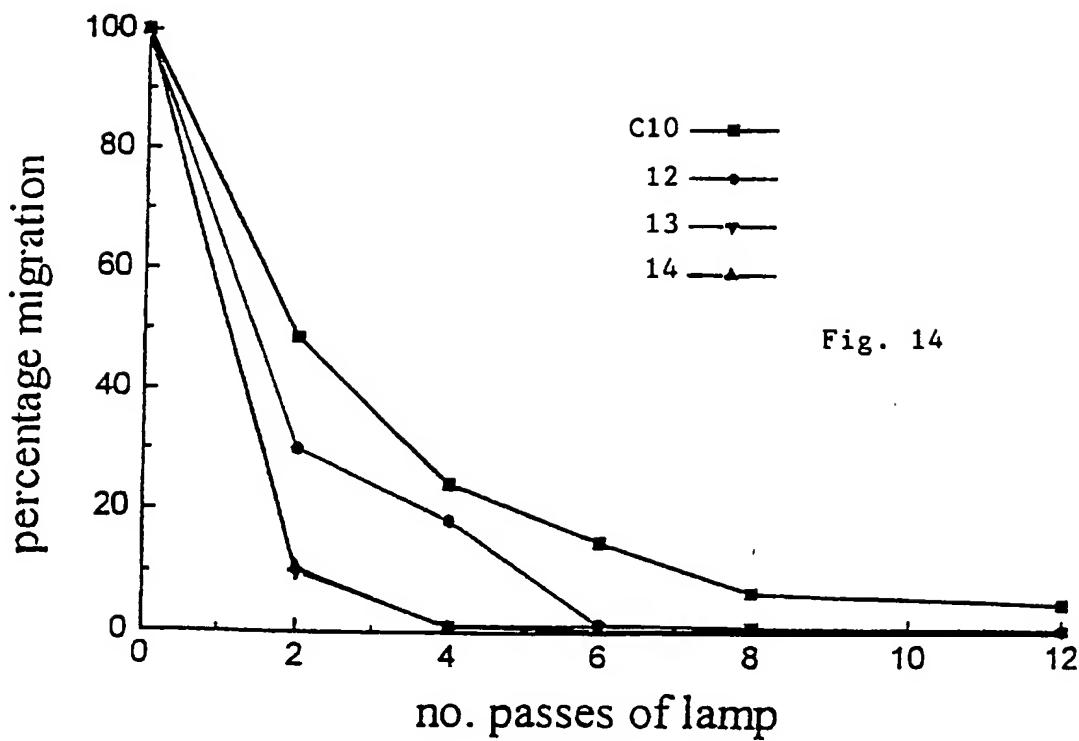


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## INTERNATIONAL SEARCH REPORT

In national Application No  
PCT/GB 97/01690

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07C69/712 C08K5/101 C08K5/06 C08K5/45 C07D335/16  
C07C49/84 C07C321/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of database and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ALAIN CASTELLAN ET AL.: "Attempts to photostabilize paper by application made from high-yield pulp by application of UV screens containing groups to aid their compatibility with cellulose and lignin" JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY, vol. 84, 1994, AMSTERDAM NL, pages 311-316, XP002043755</p> <p>* compounds 5,7 *</p> <p>see page 312</p> <p>see page 315, left-hand column, paragraph 3 - paragraph 4</p> <p>see page 315, right-hand column, paragraph 2</p> <p>---</p> <p>-/-</p>	1-6,8-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

16 October 1997

27.10.97

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## Authorized officer

Kinzinger, J

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 97/01690

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DEBORAH A. GUSTOWSKY ET AL.: "Electrochemical Switching in Anthraquinone-Substituted Carbon-Pivot Lariat Ethers and Podants: Chain Length Effects in Geometric and Electronic Cooperativity" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 108, no. 24, 26 November 1986, DC US, pages 7553-7560, XP002043756 * compounds 3 to 5 * see page 7544 see page 7559, right-hand column, paragraph 3 - page 7560, left-hand column, paragraph 1 -----	1-11

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